

# Normal-state transport properties of $\text{PrFeAsO}_{1-x}\text{F}_y$ superconductor

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(Dated: July 24, 2008)

## Abstract

We have synthesized oxygen-deficient fluorine-doped samples of nominal composition  $\text{PrFeAsO}_{1-x}\text{F}_y$  to study the normal and superconducting state properties. Resistivity of undoped  $\text{PrFeAsO}$  exhibits a strong anomaly at around 155 K due to the spin-density-wave instability. Fluorine doping ( $x=0.4$ ,  $y=0.12$ ) suppresses this magnetic instability and drives the system to the superconducting ground state with superconducting onset temperature 50 K. The behavior of normal-state resistivity changes from  $T^2$ -like to  $T$ -linear to sublinear in  $T$  with increasing temperature indicating that both electron-electron interaction and electron-phonon interaction are strong. From the analysis of  $T$  dependence of  $\rho$ , we have estimated the electron-phonon coupling strength ( $\lambda$ ) to be quite large (1.3).

PACS numbers: 71.38.-k, 74.25.Fy, 74.70.-b, 75.30.Cr

Keywords: Iron-based oxypnictide superconductors, resistivity saturation, strong electron-phonon coupling

## 1. Introduction

The recent discovery of superconductivity in iron-based oxypnictide  $\text{LaFeAsO}_{1-x}\text{F}_x$  with transition temperature ( $T_c$ ) 26 K has generated tremendous activity in this field [1, 2]. Apart from the high transition temperature, this system exhibits many interesting properties possibly due to the presence of iron. The undoped parent compound  $\text{LaFeAsO}$  is nonsuperconducting metal and shows spin-density-wave (SDW) instability below 150 K. Partial substitution of fluorine for oxygen suppresses the long-range magnetic ordering and drives the system to superconducting state above a critical value of fluorine content ( $x$ ). Immediate after the first report on superconductivity in  $\text{LaFeAsO}_{1-x}\text{F}_x$ , attempts have been made to change the composition with an aim to increase the superconducting transition temperature. Several groups have shown that the replacement of La by other rare earth elements ( $R$ ) such as Ce, Pr, Nd, Sm, etc increases  $T_c$  significantly [3, 4, 5, 6, 7].  $T_c$  as high as 55 K has been reached in  $\text{SmFeAsO}_{1-x}\text{F}_x$  [7].

Usually, two methods have been followed for the preparation of iron-based oxypnictides. Using high pressure synthesis technique, one can obtain fluorine-free oxygen-deficient  $R\text{FeAsO}_{1-\delta}$  superconducting samples [5, 8, 9]. However, samples prepared in this method contain appreciable amount of impurity phases resulting from the unreacted ingredients [5, 8, 9]. In the other method, oxygen is partially replaced by fluorine and the sample is prepared either in high vacuum or in the presence of inert gas. Though samples prepared in this method are superior in quality as compared to that obtained from high pressure synthesis, often small amounts of impurity phases are present [10, 11]. We use a slightly different method for the preparation of good quality superconducting  $\text{PrFeAsO}_{1-x}\text{F}_y$  samples. The nominal composition for this sample is oxygen deficient and oxygen is partially replaced by fluorine as well ( $x \neq y \neq 0$ ). To some extent, this is basically a combination of above two methods but the samples can be prepared in vacuum. In this sample, no impurity has been noticed from the x-ray diffraction pattern and the superconducting transition is sharp. We observe that single phase samples with  $x \leq 0.4$  can be prepared in this method.

In this paper, we report the results on structural, magnetic and transport properties of  $\text{PrFeAsO}_{1-x}\text{F}_y$  as a function of temperature. In order to extract the normal-state parameters

useful for understanding the mechanism of superconductivity, resistivity has been measured up to 475 K. The resistivity behavior above  $T_c$  shows three distinct temperature regimes wherein two different kinds of scattering processes originating from the electron-electron scattering and the electron-phonon scattering are predominant. From the analysis of high-temperature resistivity, we have estimated the electron-phonon coupling strength in this system to be large, which is consistent with the reported large value of normalized energy gap parameter  $2\Delta/kT_c=8$  [12].

## 2. Sample preparation and experimental techniques

Polycrystalline samples of nominal compositions  $\text{PrFeAsO}$  and  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  were synthesized by conventional solid state reaction method. High purity chemicals Pr (99.9%), Fe (99.998%),  $\text{Fe}_2\text{O}_3$  (99.99%), AS (99.999%),  $\text{PrF}_3$  (99.9%) and  $\text{Pr}_6\text{O}_{11}$  (99.99%) from Alfa-Aesar were used for the sample preparation. Finely grounded powders of  $\text{Pr}_{0.96}\text{As}$ , Fe,  $\text{Fe}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$  (pre-heated at 600 °C) and  $\text{PrF}_3$  were thoroughly mixed in appropriate ratios and then pressed into pellets. The pellets were wrapped with Ta foil and sealed in an evacuated quartz tube. They were then annealed at 1250 °C for 36 h.  $\text{Pr}_{0.96}\text{As}$  was obtained by slowly reacting Pr chips and As pieces first at 850 °C for 24 h and then at 950 °C for another 24 h in an evacuated quartz tube. The product was reground, pressed into pellets and then sealed again in a quartz tube and heated at 1150 °C for about 24 h. The phase purity and the room-temperature lattice parameters of the samples were determined by powder x-ray diffraction (XRD) method with Cu  $K_\alpha$  radiation. dc magnetization measurements were done using a Quantum Design Physical Property Measurement System (PPMS) at a field of 50 Oe. Resistivity was measured by standard four-probe technique up to 475 K with an excitation current 5 mA. Electrical contacts were made using conducting silver paint. Resistivity measurements above 300 K were done in vacuum in order to reduce the oxidation of the sample. Thermopower measurements were done using standard dc differential technique [13]. In this method, a small temperature gradient was created across the sample and the corresponding voltage drop was measured.

## 3. Experimental results and discussion

The XRD pattern for the fluorine-doped  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  sample is shown in Fig. 1,

which could be well indexed on the basis of tetragonal ZrCuSiAs-type structure with the space group  $P4/nmm$ . We did not observe any impurity phase within the resolution of an x-ray. The lattice parameters obtained from the Rietveld refinements are  $a=3.9711 \text{ \AA}$  and  $c=8.5815 \text{ \AA}$ . Fe-Fe bond length calculated from the refinements is  $2.8080 \text{ \AA}$ . We have also determined the lattice parameters for PrFeAsO. For this sample, both  $a$  ( $=3.984 \text{ \AA}$ ) and  $c$  ( $=8.596 \text{ \AA}$ ) are larger than that for the fluorine-doped sample. As expected, the incorporation of F in place of O reduces the size of the unit cell. The above values of lattice parameters are comparable with those reported for 12% F-doped and PrFeAsO samples, respectively [5]. We would like to mention here that the nominal oxygen-site vacancy in our present sample is  $(1 - x - y)=0.28$ . However, we are unable to determine the exact numbers of the oxygen-site vacancies from x-ray refinements because x-ray is insufficient for the accurate determination of the light atom stoichiometry. Neutron diffraction may reveal the information on oxygen-site vacancy. Nevertheless, one can prepare good quality and single phase samples using this technique.

To test the bulk nature of superconductivity, we have measured the temperature dependence of zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility for the F-doped sample at 50 Oe (Fig. 2). Both ZFC and FC susceptibilities start to deviate from the normal behavior and become negative below 48 K and, their values increase with decreasing  $T$ . The shielding and Meissner fractions were calculated from the ZFC and FC data, respectively. Assuming theoretical density  $6.96 \text{ g/cm}^3$ , a shielding fraction of 65% and a Meissner fraction of 23% are found at 5 K. These volume fractions are comparable with those (74% and 33%, respectively) observed in  $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$  at 2 K for  $H=20 \text{ Oe}$  [10]. The present values for volume fractions might enhance significantly, if the measurements could have been performed at lower fields.

Figure 3(a) shows the temperature dependence of resistivity for  $\text{PrFeAsO}_{1-x}\text{F}_y$  samples. The behavior of  $\rho(T)$  for the parent sample is qualitatively similar to that of  $\text{LaFeAsO}$  [1]. An anomalous peak associated with SDW shows up at  $T_s=155 \text{ K}$ . Below the occurrence temperature of SDW, resistivity drops steeply. Above 250 K,  $\rho$  increases linearly with  $T$ . The linear behavior is maintained up to as high as 475 K. However, at low temperature

$\rho$  exhibits a power-law behavior. For  $T < T_s$ , resistivity data can be fitted well with an expression,  $\rho = \rho_0 + aT^n$ , with  $n$  close to 1.5. Fluorine doping leads to the suppression of the SDW state. For  $y=0.12$ , the behavior of  $\rho$  vs  $T$  curve changes completely and no anomaly due to SDW formation is observed.  $\rho$  for this sample decreases monotonically with decreasing temperature until the superconducting onset temperature ( $T_c^{on}$ ) is reached below which  $\rho$  drops sharply and becomes zero just below 47 K. The inset displays the enlarged view of the onset of superconductivity. For this sample,  $T_c^{on}$  is 50 K (using the 90% criterion), and a transition width  $\Delta T_c = T_c(90\%) - T_c(10\%) = 2.7$  K. For  $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$  the value of  $\Delta T_c$  is 4.5 K [10]. Thus the superconducting transition for  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  is sharper than that for  $\text{LaFeAsO}_{1-x}\text{F}_x$  [1, 2, 10].

From the behavior of the  $T$  dependence of  $\rho$ , one can identify three distinct temperature regimes. We find that  $\rho$  above  $T_c$  exhibits a quadratic temperature dependence,  $\rho = \rho_0 + AT^2$ , in the range of  $T$  between 70 K and 170 K [Fig. 3(b)]. The  $T^2$  behavior of  $\rho$  below 170 K indicates a strong electronic correlation and is consistent with the formation of a Fermi-liquid state. The value of  $A$  determined from the fit is  $2.45 \times 10^{-5} \text{ m}\Omega \text{ cm K}^{-2}$ . This value of  $A$  is comparable with that observed in some semiheavy-fermion compounds [14] but larger than that reported for several metallic oxides [15]. Often, strongly correlated systems are characterized by the Kadowaki-Woods (KW) ratio  $A/\gamma^2$ , where  $\gamma$  is the coefficient of linear heat capacity [14]. Using the reported value of  $\gamma = 4.1 \text{ mJ K}^{-2} \text{ mol}^{-1}$  for  $\text{LaFeAsO}_{0.89}\text{F}_{0.11}$  system [10], we find that the KW ratio for the present sample is  $1.46 \times 10^{-3} \mu\Omega \text{ cm K}^2 \text{ mol}^2 \text{ mJ}^{-2}$ . This value of KW ratio is about two orders of magnitude larger than that for the heavy-Fermion system ( $1.0 \times 10^{-5} \mu\Omega \text{ cm K}^2 \text{ mol}^2 \text{ mJ}^{-2}$ ) but comparable to that for  $\text{Na}_{0.7}\text{CoO}_2$  [14, 16]. Such a large value KW ratio means that the strong electron correlations are responsible for enhancing not so much the effective mass of quasiparticles as their scattering rate. A systematic deviation from  $T^2$  to  $T$ -linear behavior of  $\rho$  is observed above 170 K. Figure 3(c) clearly shows that  $\rho$  is linear over a wide range of  $T$  above 170 K. The temperature coefficient of  $\rho$  in the linear regime is  $8.6 \mu\Omega \text{ cm K}^{-1}$ . This value of  $d\rho/dT$  is an order of magnitude larger than that observed in high temperature superconductors where  $\rho$  exhibits linear behavior up to as high as 1100 K [17]. With increasing  $T$  above 280 K,  $\rho$  increases slower than  $T$ -linear and exhibits a downward curvature. Thus the nature

of temperature dependence of resistivity for the fluorine-doped superconducting sample is very different from that of non-superconducting parent compound at high temperatures. Undoped PrFeAsO does not show any saturation-like behavior at high temperatures. The high temperature resistivity behavior of the superconducting sample is quite similar to that observed in several A15 compounds and Chevrel phases [18]. Qualitatively, this reveals that the mean free path  $l$  of the present system is comparable with that of interatomic spacing ( $a_{in}$ ) above 300 K. In metals with  $l \sim a_{in}$ ,  $\rho$  displays a strong deviation from linearity at high temperature, known as resistivity saturation. The linear behavior of  $\rho$  between 175 K and 280 K and its deviation from linearity above room temperature, are the signatures of strong electron-phonon interaction.

The temperature dependence of thermopower  $S$  for both the samples are shown in Fig. 4. In the measured temperature range,  $S$  is negative for both the samples. The negative value of  $S$  indicates electron carriers. The magnitude of  $S$  for the superconducting sample is about 3 times larger than that for the nonsuperconducting sample. For both the samples,  $S$  increases approximately linearly with  $T$  for  $175 \text{ K} \leq T \leq 280 \text{ K}$  and a systematic deviation occurs at high temperature above 280 K. This behavior is somewhat similar to the  $T$  dependence of  $\rho$  above 175 K [Fig. 3(c)]. Below 175 K,  $S$  decreases with  $T$  faster than linear and passes through a minimum at  $T_{min}$ . For the nonsuperconducting sample,  $S$  increases at a much faster rate than that for the superconducting sample below  $T_{min}$  and exhibits a sharp maximum at 120 K. This rapid increase of  $S$  below  $T_{min}$  is possibly due to the formation of SDW state. We observe that below 175 K,  $S$  for the superconducting sample can be fitted well with an expression  $S \sim (T - T_{min})^2$ . For LaFeAsO<sub>0.89</sub>F<sub>0.11</sub>,  $S$  is large and negative, and the nature of  $S(T)$  curve is qualitatively similar to that of PrFeAsO<sub>0.6</sub>F<sub>0.12</sub> sample [10]. Indeed,  $S$  for LaFeAsO<sub>0.89</sub>F<sub>0.11</sub> is slightly larger than that for the present sample and exhibits an approximate linear behavior below 35 K, as expected from Fermi liquid theory. The smaller value of  $S$  for PrFeAsO<sub>0.6</sub>F<sub>0.12</sub> may be an indication of higher Fermi energy for this sample. Due to the higher superconducting transition temperature, no linear region is, however, expected to appear for PrFeAsO<sub>0.6</sub>F<sub>0.12</sub> sample.

We now combine resistivity results with band-theory parameters in order to estimate the

strength of electron-phonon coupling ( $\lambda$ ). Expressing the resistivity in terms of plasma energy ( $\hbar\omega_p$ ) and electron-phonon scattering time ( $\tau_{ep}$ ),  $\rho(T) - \rho(0) = 4\pi/(\omega_p^2\tau_{ep}) = 4\pi v_F/(\omega_p^2 l)$ , where  $v_F$  is the Fermi velocity [17, 19]. Also, at high temperature where electron-phonon scattering dominates resistivity,  $\tau_{ep}$  is given by  $\hbar/\tau_{ep} = 2\pi\lambda kT$  [19]. From these relations we can deduce

$$\lambda = \frac{\hbar\omega_p^2}{8\pi^2 k} \frac{d\rho}{dT} \quad (1)$$

and

$$\lambda = \frac{\hbar v_F}{2\pi l k T}. \quad (2)$$

Assuming  $l \sim a = 4 \text{ \AA}$  at 300 K and the value of Fermi velocity  $v_F = 1.3 \times 10^7 \text{ cm/s}$  calculated from band theory [20], we find a large value for  $\lambda = 1.3$ .  $\lambda$  can also be estimated independently using the values of resistivity slope ( $8.6 \mu\Omega \text{ cm/K}$ ) in the linear region and plasma energy ( $\hbar\omega_p \sim 0.8 \text{ eV}$ ) determined from the inplane penetration depth [21]. In this case also  $\lambda$  is 1.3. Thus the value of  $\lambda$  calculated in two different methods is same and quite large. This suggests that electron-phonon scattering is dominating the high temperature resistivity of the superconducting sample and is consistent with the resistivity saturation.

#### 4. Conclusions

In conclusion, we have analyzed resistivity and thermopower for oxygen-deficient fluorine-doped samples of nominal composition  $\text{PrFeAsO}_{1-x}\text{F}_y$  over a wide range of temperature. Fluorine doping ( $x=0.4$ ,  $y=0.12$ ) suppresses the formation of SDW state and drives the system to the superconducting ground state with  $T_c=50 \text{ K}$ . With increasing  $T$ , resistivity above  $T_c$  crosses over from  $T^2$  dependence due to the electron-electron interaction to linear in  $T$  and then to a saturation-like behavior at higher temperature due to the electron-phonon interaction. In contrast, undoped  $\text{PrFeAsO}$  exhibits linear  $T$  dependence up to 475 K. The occurrence of saturation-like behavior indicates that the electron-phonon interaction is strong. We have estimated the electron-phonon coupling parameter  $\lambda \sim 1.3$  from the linear and sublinear dependence of  $\rho$  for the superconducting sample. This result together with reported large value of normalized energy gap parameter

$2\Delta/kT_c=8$  suggests that this system belongs to the class of strong coupling superconductors.

### **Acknowledgement**

The authors would like to thank B. Ghosh for stimulating discussions and S. K. De, M. Patra, J. Ghosh and A. Pal for the technical help during the sample preparation and measurements.



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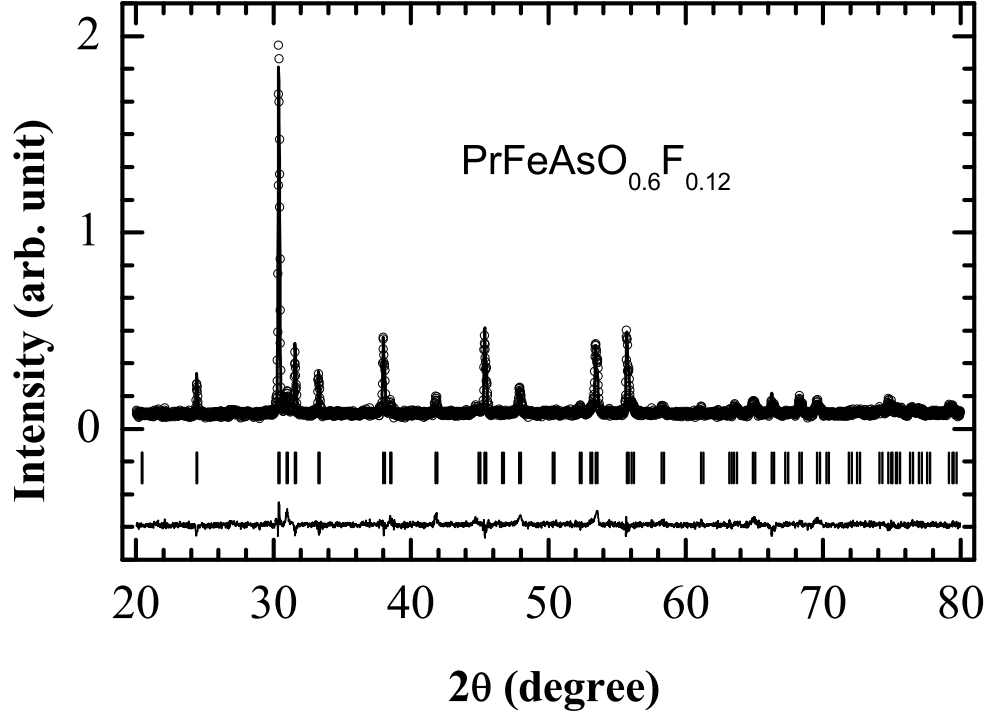


FIG. 1: The x-ray diffraction pattern for the superconducting  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  sample. The solid line corresponds to Rietveld refinement of the diffraction pattern with  $P4/nmm$  space group.

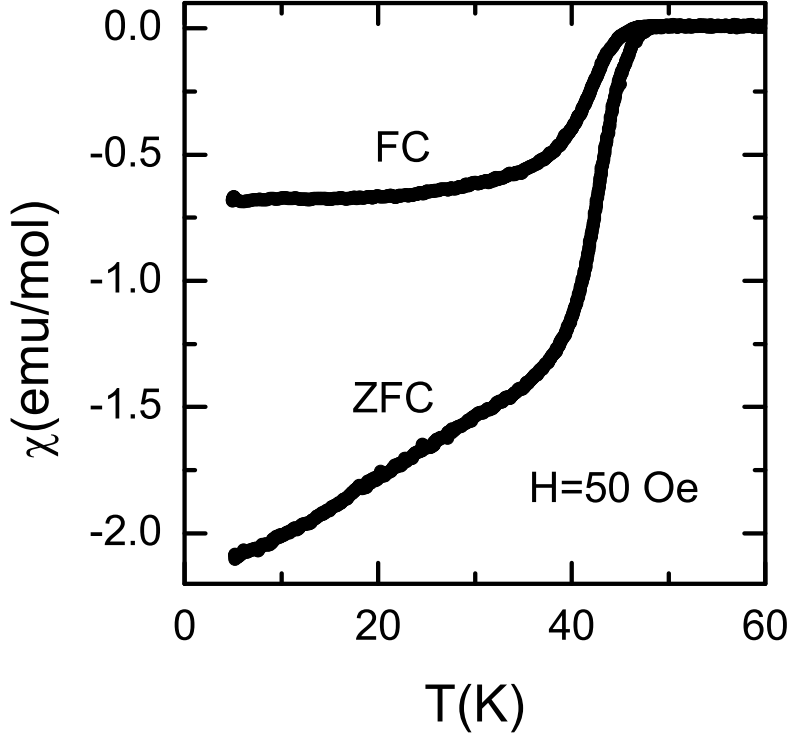


FIG. 2: Temperature dependence of FC and ZFC dc magnetic susceptibility ( $\chi$ ) measured at a field of  $H=50$  Oe for  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  sample.

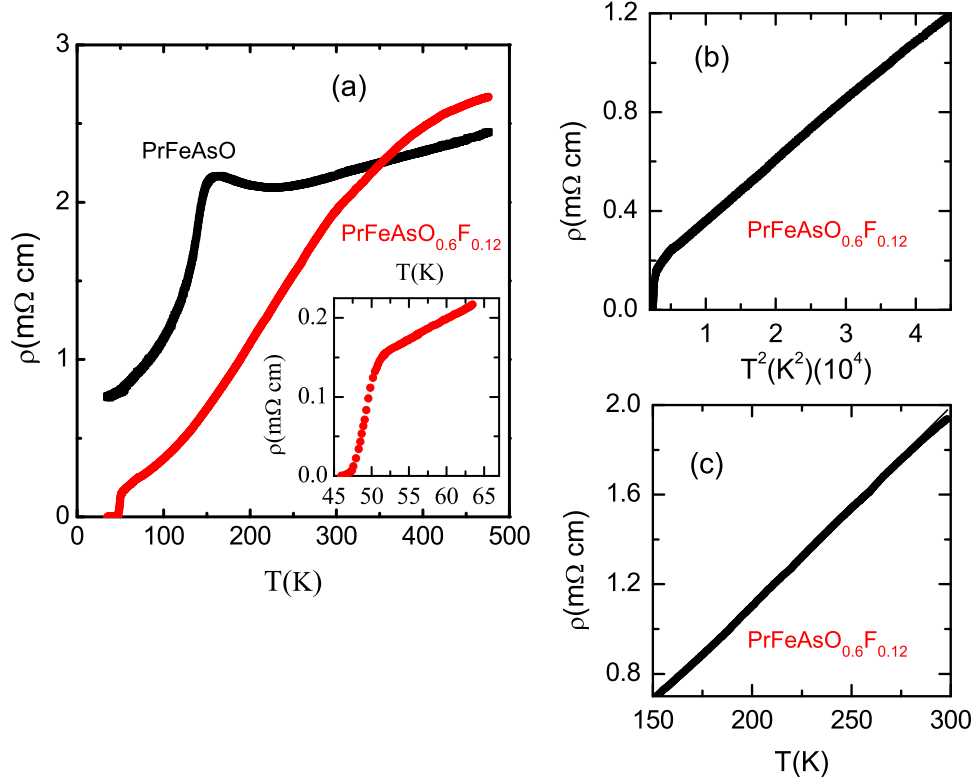


FIG. 3: (a) Temperature dependence of resistivity ( $\rho$ ) for  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  and  $\text{PrFeAsO}$  samples. Inset (a): Enlarged view of resistivity change close to the superconducting transition temperature. (b)  $T^2$  dependence of  $\rho$  for superconducting  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  sample in the range  $70 \text{ K} \leq T \leq 170 \text{ K}$ . (c) Linear behavior of  $\rho$  for  $175 \text{ K} \leq T \leq 280 \text{ K}$  for  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  sample

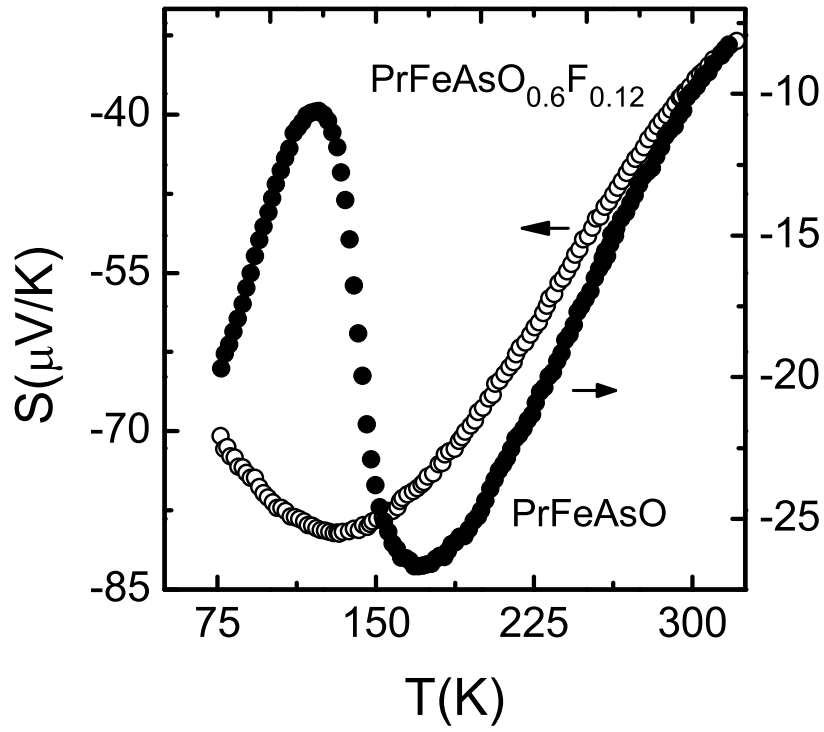


FIG. 4: Temperature dependence of thermopower ( $S$ ) for  $\text{PrFeAsO}_{0.6}\text{F}_{0.12}$  (open symbol) and  $\text{PrFeAsO}$  (solid symbol) samples.